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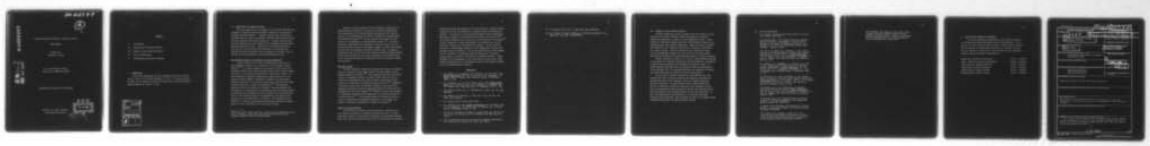

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Computer Simulation Studies of Molecular Solids

FINAL REPORT

Sidney Yip

February 13, 1978

U. S. Army Research Office
Contract No. DAHC04-74-C-0036

Massachusetts Institute of Technology

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I. INTRODUCTION

This report summarizes the work performed during the contract period, July 1, 1974 through November 30, 1977. It should be noted a number of the studies are being continued under a new ARO contract which commenced on January 1, 1978.

II. DESCRIPTION OF PROBLEMS STUDIED

The basic objective of the project was to develop and apply the technique of computer molecular dynamics simulation to problems in materials science research. Computer programs were developed for the simulation of atomic and molecular solids in which atoms interact through continuous interatomic potentials. Computer programs also have been developed for the simulation of hard-sphere mixtures which undergo chemical reactions. Applications of these programs have been made to study the structure and motions of grain-boundary systems, molecular vibrations and reorientations in solids, and instabilities in multicomponent systems undergoing reactions.

Equilibrium Properties and Dynamics of Grain Boundaries*

A basic problem in the study of thermodynamic properties of grain-boundary systems is the calculation of the boundary surface tension.(1) At a given temperature the surface tension can be expressed in terms of the excess internal energy and the excess entropy (relative to the reference system which is the perfect solid). We have developed a method for computing the vibrational part of the entropy by using computer simulation to generate the vibrational frequency spectrum of the boundary system and to evaluate the system internal energy over a range of temperature.(2) The frequency spectrum is used to calculate the entropy in the quasiharmonic approximation at a sufficiently low temperature where the approximation is valid, and the additional entropy is obtained by integrating the ratio of the internal energy to the temperature from this low temperature up to the temperature of interest. This method has been applied to a 400-atom three-dimensional system containing two large-angle tilt grain boundaries and a structural vacancy.

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*This part of the project has been carried out in collaboration with Drs. G. Bishop, A. Cox, and R. Harrison of Army Materials and Mechanics Research Center, Watertown, Mass.

Motions of grain boundaries are of fundamental importance in understanding the behavior of materials at elevated temperatures. The coupled motion of boundary sliding and migration has been discussed in the literature on the basis of theoretical considerations and bubble-raft models.[3] We have observed this process in the course of our simulation of grain-boundary systems.[4] A series of simulation experiments were performed to study the effects of temperature, initial stress on the system, number of atoms in the system, and the type of interatomic potential function used. In addition, simulations were carried out on two-dimensional grain-boundary systems which do not contain any structural vacancies and recrystallization of the solid was observed as a competing process to boundary sliding and migration.

Molecular Solids

We have developed a simulation program which treats a molecular solid as a system of atoms which interact through bonding and nonbonding potential functions.[5] This program evolved from an earlier version of simulation program for atomic solids which was used to compute the thermodynamic and lattice dynamic properties of solid argon over a wide range of temperatures and pressures.[5] Simulation of molecular solids thus far has been confined to α-N_2 where time-dependent correlation functions describing molecular vibrations and reorientations have been computed.[6] Recently a study was initiated to investigate the vibrational relaxation of a diatomic molecule in an atomic lattice.[7] It is expected that this work will lead to a study of dissociation/recombination dynamics, in particular, the problem of geminate recombination in gases and liquids.[8]

Chemical Reacting Systems

The technique of computer molecular dynamics largely has not been applied to problems of chemical reactions thus far. We have performed a number of exploratory calculations on hard-sphere systems which show that the important features such as interspecies conversion,

spontaneous decay, and release of internal energy of a molecule during collisions all can be simulated in a computer molecular dynamics experiment. In particular we have obtained computer results useful for testing the validity of conventional macroscopic rate equations.[9] The computer program used in this work is an adaptation of a program[10] written originally to study hydrodynamic flow processes and was effectively a program for two-dimensional systems. We have recently generated a corresponding program for three-dimensional systems with periodic boundary conditions. One of the applications of this program will be the study of collision-induced de-excitation of internal energy states as a model of the process of thermal explosion. Other problems to be investigated in the continuation of this work include chemical instabilities in multicomponent systems and dynamical properties of diffusion-reaction systems.

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2. R.J. Harrison, J.A. Cox, G.H. Bishop, and S. Yip, Nuclear Metallurgy, Vol. 20, Parts 1 and 2, R.J. Arsenault, J.R. Beeler, and J.A. Simmons, Eds. (National Bureau of Standards, 1976), p. 604.

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7. A study of vibrational relaxation in liquids has been reported by D.L. Jolly, B.C. Freasier, and S. Nordholm, Chem Phys. 21, 211 (1977).

8. Atom recombination has been studied using computer simulation by A.J. Stace and J.N. Murrel, Mol. Phys. 33, 1(1977).

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III. SUMMARY OF MOST IMPORTANT RESULTS

The most significant result to emerge from our research are the observations of grain boundary sliding and migration in finite-temperature simulation of three- and two-dimensional solids. These results are the first demonstration that grain-boundary motions can be simulated under fully dynamic conditions. They also serve to confirm the validity of the concept of "DSC lattice" vectors of coincidence site lattice theory. Detailed analysis of the simulation results provide considerable insight into the effects of the local strain generated by the defect in determining the behavior of grain boundaries.

Another significant result of our study of grain-boundary systems is the method for computing vibrational entropy through the vibrational frequency spectrum without the assumption of harmonic forces. By using computer simulation data in conjunction with the techniques of lattice dynamics one can considerably extend our capability of analyzing defect structures in solids at elevated temperatures.

In the area of chemical reactions we have provided the first demonstration that reactions involving interspecies conversion and spontaneous decay can be studied in detail by computer molecular dynamics simulation. We have obtained results which showed that multiple steady-state solutions predicted by the analysis of macroscopic rate equations indeed occur and that the rate equations give a good description of the average behavior of the reacting system. We have also demonstrated the feasibility of simulating exothermic reactions with thresholds, thus providing the basis for studying energy dissipation mechanisms in highly unstable systems.

IV. LIST OF PUBLICATIONS

O.L. Deutsch, "Computer Simulation Studies of Solids", Ph.D. Thesis, MIT (1975).

O.L. Deutsch and S. Yip, "Computer Molecular Dynamics Studies of Solids", Proceedings of the 11th Annual Meeting of the Society of Engineering Science, Inc., November 11-13, 1974, Duke University, Durham, North Carolina. (Abstract only)

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R.J. Harrison, G.H. Bishop, S. Yip, and T. Kwok, "Computer Molecular Dynamic Studies of Grain Boundary 'Brownian Motion'", paper to be presented at the Spring Meeting of the American Physical Society, Washington DC, April, 1978.

V. PARTICIPATING SCIENTIFIC PERSONNEL

All the personnel who participated in the contract research are listed below along with their period of participation. In addition, it should be noted that the study of grain-boundary systems was carried out in collaboration with Drs. G.H. Bishop, J.A. Cox, and R.J. Harrison, scientists at the Army Materials and Mechanics Research Center, Watertown, Massachusetts.

Sidney Yip, Principal Investigator	7/1/74 - 11/30/77
Owen L. Deutsch, Associate Investigator	9/1/75 - 11/30/77
Peter Ortoleva, Research Associate	9/1/74 - 5/31/75
Thomas Kwok, Research Assistant	9/1/75 - 11/30/77
Dong-Pao Chou, Graduate Student	9/1/77 - 11/30/77
Hashem Akbari, Graduate Student	2/1/76 - 12/31/76

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This report gives a summary of the problems studied, namely, thermodynamic properties and motions of grain boundaries, dynamics of molecular solids, and chemical reactions in model systems, and a brief description of the most significant results..

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